

surface. However, the surface roughness of the metal substrate should not be such as to provide mechanical interlocking between the metal and the ultimate glass coating. Uncontrolled rough surfaces will result in residual thermo-mechanical stresses and strains upon cooling.

Any oxidizing atmosphere capable of initiating a chemical reaction involving an electron transfer process between the active oxidizing agent in the atmosphere and the metal may be employed for oxidation. Obviously, the oxidation process will vary depending upon the particular metal and oxidizing atmosphere employed. However, it has been found that subjecting a stainless steel surface to air at about 800° C. for about 20 minutes will result in a sufficiently thick oxidation layer to properly enhance the ion-diffusion bonding of the bioglass to the metal surface.

As noted above, the metal must be heated to that temperature at which the volume expansion of the metal equals that of the glass at the temperature (T_g) where the volume expansion of the glass becomes non-linear and subsequently immersed in a molten bioglass for a relatively short period of time, i.e., less than about 5 seconds, in order to provide an adherent coating on the metal surface but insufficient to allow substantial heating of the metal substrate above T_1 . The time of immersion may be as low as about 2 seconds.

The viscosity of the molten bioglass composition is easily controlled due to its alkali content by merely varying the temperature thereof in increments of 10° C. to 25° C. By varying the viscosity of the molten bioglass, the thickness of the adherent coating on the metal substrate may be effectively controlled. Generally, the process is controlled so as to provide a bioglass coating thickness of about 0.2 mm to about 2 mm on the metal substrate, depending on the particular application of the coated substrate.

Artificial prostheses and orthopedic or dental devices constructed from the bioglass coated metal substrates of the invention are applicable as cement-free implants which are extremely strong and resistant to body fluids.

EXAMPLE 1

A structure designed as a replacement for a total hip joint in a monkey composed of stainless steel having the composition.

| | Wt% | |
|----|------|------------------------|
| C | 0.03 | Impurities (P,S) < 0.3 |
| Mn | 1.5 | Fe - balance |
| Si | 0.5 | |
| Cr | 18 | |
| Ni | 13 | |
| Mo | 2.25 | |

was thoroughly cleaned by sandblasting with 180 grit alumina at 80 psi to remove foreign scale and roughen the surface to about a 150 μ m finish. The roughening increases the surface area of the metal substrate thereby providing more area for a diffusional bond between the glass and metal.

The device is then thoroughly cleaned ultrasonically in acetone three times (at least 10 minute cycle). The device is then suspended in the center of a tubular oxidizing furnace open to the atmosphere and maintained at 800° C. (T_1). The device was allowed to remain in the furnace for 20 minutes to allow for complete linear

expansion and to provide an oxide finish in the roughened metal surface of about 1-2 μ m in thickness.

A biologically active glass having the composition of Bioglass A above was melted in a platinum crucible for a period of 1 hour at 1325° C. The volume of molten glass is sufficient to allow complete immersion of the steel device. The glass is very fluid at this temperature and has a viscosity of about 2 poise.

The metal device and crucible containing the bioglass are simultaneously withdrawn from their respective furnaces. The metal device is immediately immersed in the molten bioglass with a quick, smooth motion and withdrawn at a rate of about 2 cm/sec. This produces a fluid coating of glass of about 1 mm in thickness in the surface of the device. The entire procedure requires about 3-5 seconds. Obviously, variations in the thickness of the bioglass layer may be achieved by controlling the viscosity of the glass, the length of time of residence of the device in the molten glass, and the rate of withdrawal of the device from the glass.

The glass coated device is held in the air for 20 to 30 seconds to allow the surface temperature of the glass to reach about 800° C. During this period the glass flows thereby relieving any induced stresses. Also during this period diffusion of metal from the thin oxide layer into the first few (5) micrometers of glass occurs.

After the temperature of the surface of the glass has cooled to about 700° C., the coated device is placed in a cooling furnace and allowed to cool to room temperature thereby permitting uniform contraction of the glass and metal.

Optionally, the coated device may be re-heated to 500°-700° C. or allowed to remain at 500°-700° C. after coating for a pre-determined period of time to allow for partial or full crystallization of the glass.

EXAMPLE 2

The above procedure is followed employing a similar device composed of the same stainless steel and a bioglass having the composition of Bioglass B above. The temperature of the molten glass is about 1150° C. The resulting coated device was suitable for use as a prosthetic device.

EXAMPLE 3

The above procedure was employed utilizing the bioglass composition of Example 1 and a titanium metal device. The metal device was initially heated to 900° C. in an argon atmosphere with a small partial pressure (< 1mm) of oxygen prior to immersion. The atmosphere composition is controlled so as to prevent the oxide layer on the metal from becoming too thick.

Polished surfaces of the interfaces between the metal substrates and glass coatings of Examples 1, 2 and 3 were analyzed by energy dispersive X-rays which revealed that a true chemical or diffusional bond had matured between the glass and metal.

What is claimed is:

1. A method of bonding a bioglass layer to a metal substrate comprising:

- (1) heating a metal substrate having a roughened, oxidized surface to about a maximum temperature (T_1) where said T_1 is selected such that the total volume expansion of said metal is substantially equal to that of said bioglass at the temperature (T_g) at which the temperature dependence of the volume of said bioglass becomes non-linear,